COMBUSTION REACTIVITY OF LOW RANK COAL CHARS

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Introduction

For many years the CSIRO has been involved in studies on the combustion kinetics of coal chars and related materials. Early work included studies on a char produced from a Victorian brown coal (1). More recently, the combustion kinetics of chars produced during the flash pyrolysis of sub-bituminous coals have been determined (2,3).

In this paper data are given for the combustion reactivities of four flash pyrolysis chars. Their reactivities are compared with the results for chars produced from low and high rank coals, and petroleum coke. Reactivity is expressed as the rate of combustion of carbon per unit external surface area of the particle, with due correction being made for the effect of the mass transfer of oxygen to the particle.

Experiment and Theory

Details of the method of producing the flash pyrolysis chars are available elsewhere (4), as is information on the procedure for measuring their combustion rates (2,3,5). In brief, pulverized Millmerran and Wandoan coals (Queensland, Australia) were flash pyrolysed at various temperatures between 500 and 800°C. The resulting chars were screened to yield a size fraction having a median mass size around 80 μm. The properties of the chars are presented in Table 1.

TABLE 1 Properties of the Chars

	Millmerran					Wandoan
Pyrolysis temperature, °C	540	585	610	780	800	550
Median mass size, μm	85	76	90	70	88	76
Size below which 90% of material lies, μm	100	95	118	92	98	96
Size below which 10% of material lies, μm	66	52	61	47	74	49
Particle density, g/cm^3	0.88	0.80	0.78	0.99	0.78	1.05
Chemical analysis, % w/w (as received)						
Moisture	2.7	2.2	3.3	2.5	4.7	2.9
Ash	28.0	30.4	35.6	60.1	38.2	22.1
Elemental composition						
C	56.6	55.3	50.7	31.3	50.3	60.3
H	3.8	2.8	2.7	1.1	1.3	3.3
N + S + O	8.9	9.3	7.7	5.0	5.5	11.4

Rate measurements were carried out, using an entrainment reactor, on flowing suspensions of particles in preheated oxygen-nitrogen. From progressive changes in gas composition and gas and wall temperatures along the reactor, the rate of carbon burned per unit external area of particle (ρ) was calculated.

From ρ, the chemical rate coefficient, R_c, was evaluated (6):

$$\rho = R_c \, [p_g \, (1 - \chi)]^n \qquad g/cm^2s \qquad (1)$$

where p_g is the partial pressure of oxygen in the bulk gas, n is the order of reaction in relation to p_g and λ is the ratio of ρ to the maximum possible (i.e. mass transfer limited) burning rate calculated from known physical properties (6,7).

R_c, as will be shown, is strongly dependent on particle temperature, T_p. This temperature is calculated from a heat balance over the burning particle (6).

Results and Discussion

Combustion rate data for Millmerran and Wandoan chars are shown in Arrhenius form in Fig. 1. Data for Millmerran chars produced at 585 and 610°C were combined into a single set, as were the data for the chars produced at 780 and 800°C. Rate data for other chars (derived from low and high rank coals) and also for petroleum coke are also included in Fig. 1. To permit the comparison of results for different materials exhibiting different values of n, the rate data were calculated from the relation:

$$\rho_c = R_c \, p_g^{\,n} \qquad g/cm^2s \qquad (2)$$

where p_g is taken as 1 atm. Values of the Arrhenius parameters, A (pre-exponential factor) and E (activation energy), together with the magnitude of n for each material referred to in Fig. 1 are listed in Table 2.

TABLE 2 Kinetic Data for the Combustion of Chars and Coke

Material	A $g/\{cm^2s\ (atm\ O_2)^n\}$	E kcal/mol	n	Reference
Millmerran char (540°C)	15.6	17.5	0.5	2
Millmerran char (585 and 610°C)	22.3	18.8	0.5	3
Millmerran char (780 and 800°C)	73.3	21.7	0.5	3
Wandoan char (550°C)	39.1	18.3	0.5	3
Yallourn brown coal char	9.3	16.2	0.5	1
New Zealand bituminous coal char	8	16.0	1.0	7
Anthracites and semi-anthracites	20.4	19.0	1.0	8
Petroleum coke	7.0	19.7	0.5	5

The data exhibit several notable features:

(1) The combustion rates of all the materials show a strong dependence on temperature, the values of the activation energies ranging from 16.0 to 21.7 kcal/mol.

(2) The activation energy increases and the reactivity of Millmerran chars decreases with increasing pyrolysis temperature.

(3) The most reactive char is that produced from Wandoan coal at 550°C. This material is about twice as reactive as chars produced from other low rank coals (Millmerran and Yallourn) and high rank coals (New Zealand bituminous, anthracites and semi-anthracites), and about ten times as reactive as petroleum coke.

(4) The low rank coal chars and petroleum coke show an order of reaction of 0.5. Earlier determinations on chars from high rank coals indicate a value of unity. However, a reanalysis (5) of an earlier set of data (9) showed, in the case considered, little to choose between n equal to 0.5 or 1.0.

The values of the activation energy for the Millmerran and Wandoan chars (~ 20 kcal/mol), together with those of the other materials listed in Table 2, imply reactions under circumstances where pore diffusion as well as chemical reaction exercises strong rate control, i.e. regime II (10) conditions apply. Confirmatory evidence that these materials are indeed burning under regime II conditions is provided by the steady decrease in particle size and slight reduction in the particle density of the particles as they burn away (6). This behaviour is illustrated in Fig. 2 by the data on the lowest temperature chars produced from Millmerran and Wandoan coal. Also shown are some theoretical curves indicating the changes in particle size and density to be expected for combustion at constant particle density or at constant particle size (6).

Conclusions

It has been shown that the reactivities to oxygen of chars produced from Millmerran sub-bituminous coal decrease with increasing pyrolysis temperature but are similar in magnitude to the reactivities of chars derived from a brown and a bituminous coal and to the reactivities of anthracites and semi-anthracites. However, Wandoan char, also of sub-bituminous origin, exhibits about twice the reactivity of Millmerran char and about ten times the reactivity of petroleum coke. On the basis of observed activation energy values, particle size and particle density behaviour it is concluded that the combustion rates of Millmerran and Wandoan chars are controlled by the combined effects of pore diffusion and chemical reaction.

Acknowledgements

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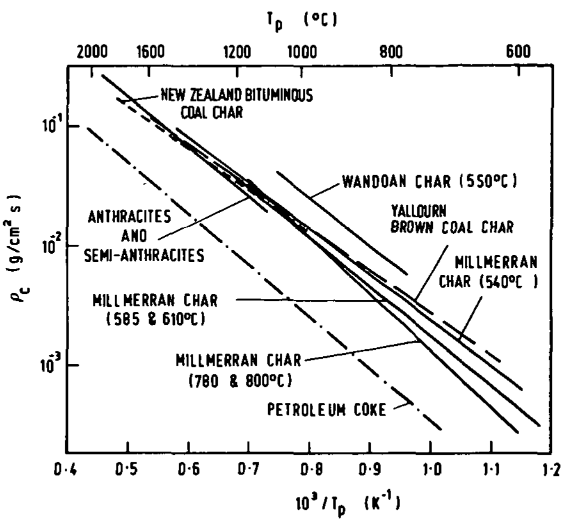

Figure 1 Combustion rate data for chars and coke

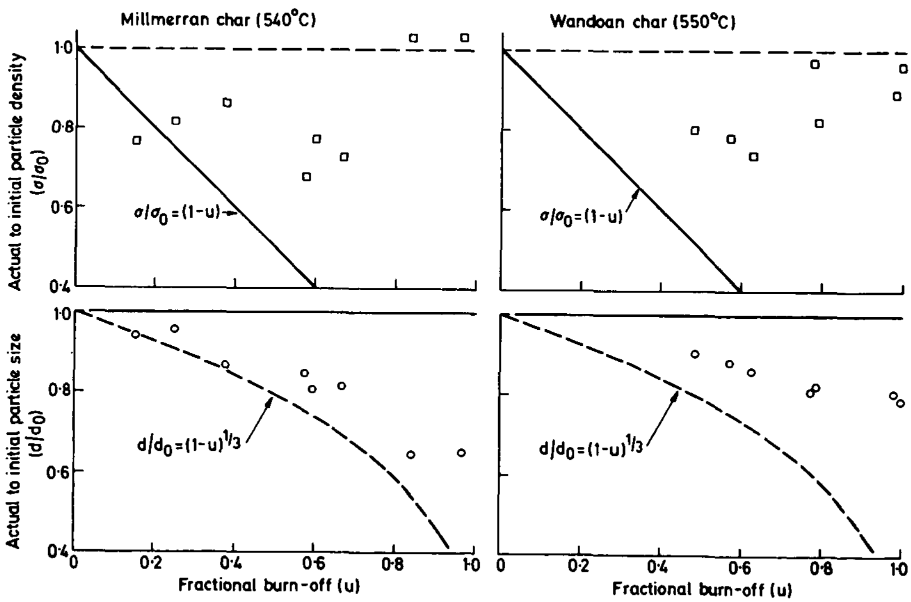

Figure 2 Burning behaviour of Millmerran and Wandoan chars (--- theoretical lines for particles burning with constant density, —— theoretical lines for particles burning with constant size)